Journal of Alloys and Compounds 764 (2018) 333–340

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Synthesis of Cu_7S_4 nanoparticles: Role of halide ions, calculation, and electrochemical properties

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ARTICLE INFO

Article history:
Received 20 February 2018
Received in revised form
23 May 2018
Accepted 7 June 2018

Keywords:
Cu_7S_4
Density functional theory calculation
Morphology control
Halide ions
Li battery

ABSTRACT

Copper sulfide (Cu_7S_4) nanoparticles were synthesized by adding ethanolic elemental sulfur solution to an aqueous solution containing Cu(II) precursor, branched polyethyleneimine (BPEI), and ascorbic acid. By varying the Cu(II) precursor used, we could control the morphology of the nanoparticles produced to be either quasi spherical (CuF_2, $Cu(NO_3)_2$, and $CuSO_4$) or vine like nanofibers ($CuCl_2$ and $CuBr_2$). By comparing experimental results and conducting calculations we found that selective adsorption of Br^- and Cl^- onto specific crystal facets and slowing of the reaction rate owing to formation of Cu(I)–anion –BPEI complexes explain the observed change in morphology from spherical particles to vine like nanofibers. We also found that the differences in morphology of Cu_7S_4 nanoparticles affects the electrochemical performance of Li batteries including the nanoparticles as electrode materials.

1. Introduction

Research on methods to synthesize inorganic nanoparticles with morphology control, including metal, metal sulfide, and metal oxide materials, has attracted increasing attention recently because nanoparticles' morphologies critically influence their physical, optical, and chemical properties [1–4]. In recent decades, the development of synthetic methods for one-dimensional (1D) nanoparticles (including nanofibers, nanowires, and nanorods) and two-dimensional (2D) nanoparticles (including nanoplates, nanodisks, and nanosheets) has progressed greatly under the use of wet chemical bottom-up approaches [5,6]. Introducing appropriate stabilizers (surfactant molecules and/or additives) can control the final morphology of nanoparticles by inducing selectivity in adsorptions to specific crystal facets [7,8]. In addition, highly kinetics-driven processes have also been applied for the formation of anisotropic nanoparticles instead of those driven by thermodynamic equilibrium [9,10].

Copper sulfide $Cu_{2-x}S$ (x: 1–2) is a well-known p-type semiconductor that has attracted attention due not only to the low cost of its precursors but also its many useful properties and its vast potential applications including those in photothermal therapy, optoelectronics, catalysis, and batteries [11–14]. For example, Chen and coworkers reported deep tissue photoacoustic imaging–guided photo thermal therapy by using near-infrared adsorption of monodisperse $Cu_{2-x}S$ nanodots [15]. The Hu research group also demonstrated that hollow Cu_7S_4 nanocrystals are effective in sensing of cancer cells [16]. In addition, $Cu_{2-x}S$ nanocrystals have been regarded as a potential candidate for applications in photovoltaics, Li batteries, and supercapacitors due to their broad absorption ability and inherent p-type transport properties [17–21]. Zhong and coworkers applied $Cu_{2-x}S$ nanocrystals to thin film photovoltaic devices [20]. Salavati-Niasari and coworkers also reported enhancement of solar cell efficiency up to 37% by using $Cu_{2-x}S$ nanocrystals [21].

There have been many wet chemical synthetic methods for the fabrication of $Cu_{2-x}S$ nanoparticles in various shapes including nanodots, nanosheets, nanodisks, and nanowires [22–25]. However, these often include the use of various organic solvents such as octadecene, oleic acid, oleyamine, and trioctylphosphine oxide, because the Cu(I)X compounds (X = Cl, Br, I) that are typically used

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https://doi.org/10.1016/j.jallcom.2018.06.082
0925-8388/

as the Cu precursors have very low solubility and are unstable in the aqueous phase [24,25]. Therefore, the development of a new method for aqueous-phase synthesis of $Cu_{2-x}S$ nanoparticles is demanded for mass production of nanoparticles. We previously reported an aqueous-phase synthesis of CuS nanofibers [23]. As a further development of this research, we decided to study how halide ions were involved in the growth of $Cu_{2-x}S$ nanofibers. There have also been some reports by other groups regarding shape control of CuS nanoparticles using halide ions. The Tao group reported that a method typically producing disk like CuS nanoparticles instead produced triangular nanoprisms when halide ions were present [24]. Donega and coworkers reported that a method to produce spherical $Cu_{2-x}S$ nanocrystals instead produced hexagonal nanosheets with addition of Br^- and triangular nanoplates with addition of Cl^- [25]. Unfortunately, these studies mentioned above merely reported experimental results. We tried to investigate such variations in morphology through both experiments and calculations.

In this research, we performed aqueous-phase synthesis of Cu_7S_4 nanoparticles having nanofiber and quasi spherical shapes. To obtain a Cu precursor stable in the aqueous phase, we used Cu(II) salts as precursors and ascorbic acid as a reducing agent to accelerate the reaction to form Cu_7S_4. By comparing experimental results and conducting calculations, we found that selective adsorption of Br^- and Cl^- onto specific crystal facets and slowing of the reaction rate by formation of Cu(I)–anion–BPEI complex explain the observed morphology change from spherical particles to vine like nanofibers. We also showed that the Cu_7S_4 nanoparticles of different morphologies have different electrochemical performance when used in Li batteries.

2. Experimental section

2.1. Materials

Branched polyethyleneimine (BPEI, MW = 750,000, 50 wt% solution in water), cupric fluoride (CuF_2), cupric chloride ($CuCl_2$), cupric bromide ($CuBr_2$), cupric nitrate ($Cu(NO_3)_2$), cupric sulfate ($CuSO_4$), ascorbic acid ($C_6H_8O_6$, purity ≥99%), sodium chloride (NaCl), sodium bromide (NaBr), sulfur (S), and ethanol (C_2H_5OH) were purchased from Aldrich and were used without further purification.

2.2. Synthesis of Cu_7S_4 nanoparticles

Synthesis of Cu_7S_4 nanoparticles was conducted in vials of volume 80 mL. First, 10 mL of Cu(II)-BPEI solution was prepared by mixing Cu^{2+} (0.033 M) with BPEI (0.04 g mL^{-1}) at 60 °C. Then, 10 mL of ascorbic acid solution (0.6 M) and 20 mL of ethanolic S solution (0.0093 M) were injected into the reaction vessel sequentially and 5 min apart. The final concentration of Cu^{2+} ions in the solution was 0.0082 M. The vessel was allowed to stand for 20 min at 60 °C and then the products were collected by centrifugation. The initial molar ratio of Cu(II) to S was held constant at 1.77 among all experiments.

2.3. UV-absorption measurement for detecting concentration of Cu(II)-BPEI complex

Two solutions with the same initial concentration of Cu(II) were prepared and labeled A and B. Solution A had 20 mL of Cu(II)/BPEI solution (0.016 M), and solution B was made by mixing 10 mL of Cu(II)/BPEI solution (0.033 M) and 10 mL of ascorbic acid solution (0.6 M). Both solutions were heated at 60 °C for 20 min, and then their UV–vis absorption spectra were acquired. The absorption curve of solution A was used as a reference curve. The absorption intensity of solution B was less due to reduction of the amount of Cu(II)-BPEI complex formed, or reaction of Cu(II)-BPEI complex and ascorbic acid to form Cu(I)-BPEI complex. The proportion of Cu(I)-BPEI complex in the solution was calculated as follows.

$$\mathrm{Cu(I)-BPEI\%} = \frac{\mathrm{Intensity(A)} - \mathrm{Intensity(B)}}{\mathrm{Intensity\ (A)}} \times 100\%$$

2.4. Density functional theory calculations

Density functional theory (DFT) calculations were performed by using the DMol [3] program in the Materials Studio 2018 software package [26–28]. The Perdew–Burke–Ernzerhof functional generalized gradient approximation was used to describe the exchange–correlation potentials of electrons [29]. Spin-unrestricted calculations were performed by using the basis set (DNP 4.4) with all electron core treatment. The convergence criteria for the geometry optimization were respectively 2.0×10^{-5} Ha, 0.004 Ha $Å^{-1}$, and 0.005 Å for energy, force, and displacement. The self-consistent field convergence was less than 1.0×10^{-5} Ha, and the electron smearing value was set to 0.005 Ha. All calculations were performed under an implicit environment by using the conductor-like screening model (COSMO) method [30]. Based on the relative permittivity at 20 °C of water (80.1) and ethanol (24.5), we calculated the relative permittivity of their 1:1 mixed solvent system (46.95) by using a mixing rule [31,32].

2.5. Model systems

DFT calculations were performed by using the $Cu_{116}S_{64}$ model, which has the same XRD pattern and structure as the experimentally synthesized roxbyite (Fig. S1) [33,34]. Based on Mumme et al.'s publication on roxbyite crystal structure and the spacing of the plane (Fig. S2) [33,34], we found that the side (0 16 0) and top (16 0 0) surfaces of the experimentally synthesized roxbyite corresponded respectively to the (0 0 1) and (1 0 0) surfaces in the $Cu_{116}S_{64}$ model. To enforce nonpolar surface systems, we made the top and bottom surfaces of the slabs symmetric. Also, the total number of atoms and the stoichiometric ratio in each surface system were taken to be the same as those of the bulk system (*i.e.*, $Cu_{116}S_{64}$). All model systems had a vacuum region extending 20 Å above the surface and were fully relaxed with energy optimization. As capping agents, NO_3^-, SO_4^{2-}, and halide ions (*i.e.*, Cl^-, Br^-, I^- and F^- ions) were considered. For BPEI, the primary propylamine was used to represent the BPEI molecule because the primary amine showed a higher binding energy with Cu atoms than secondary and tertiary amines (Fig. S3).

2.6. Characterization

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were acquired by using a JEM-2100 F microscope operating at 200 kV. Scanning electron microscopy (SEM) images were measured by using a LEO SUPRA 55 microscope. Powder X-ray diffraction (XRD) patterns were acquired by using a Rigaku D-MAX/A diffractometer operated at 35 kV and 35 mA. X-ray photoelectron spectroscopy (XPS) data were analyzed by using a Thermo Scientific K-Alpha spectrometer. Fourier transform infrared spectra were acquired by using a Jasco FTIR-6100. The concentrations of Cu(II)/BPEI and Cu(I)/BPEI in the solution were determined from UV–vis spectra (Agilent, Cary 60).